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AMBIENT ATMOSPHERIC HYDROCARBON CONTENT AS DETERMINED BY GAS CHROMATOGRAPHIC TECHNIQUES FOR RURAL TIDEWATER VIRGINIA IN LATE SPRING 1974

(NASA-CR-147922) AMBIENT ATMOSPHERIC HYDROCARBON CONTENT AS DETERMINED BY GAS CHROMATOGRAPHIC TECHNIQUES FROM RURAL TIDEWATER VIRGINIA IN LATE SPRING 1974 (Old Dominion Univ., Norfolk, Va.) 13 p HC $3.50 G3/45

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INTRODUCTION

In an attempt to ascertain the naturally generated hydrocarbon contribution to the air quality of the Hampton Roads region of Tidewater Virginia, a series of 27 air samples was obtained in two rural locations during late spring of 1974. These samples were analyzed for their hydrocarbon content (carbon number range C_5 to C_{10}) using gas chromatographic techniques. Thirty different hydrocarbon species were identified and monitored in the experiment. Preliminary analysis of the data indicates an average concentration of 397 parts per billion by weight (carbon) for the total non-methane hydrocarbon loading for C_5 to C_{10} during the experiment.

This value exceeds the National Primary Air Quality Standards as set by the Environmental Protection Agency (0.24 ppm - 160 $\mu g/m^3$). The largest contribution to the measured concentrations was found to be the paraffin series of hydrocarbons. The largest average concentration of any of the 30 molecules identified was cyclopentane (188 ppb by weight C).

EXPERIMENT

1. Sampling and Analysis Techniques

The sampling container was made of a stainless steel cylinder (volume about 1 liter - see fig. 1). Attached to this cylinder were two high-vacuum Swagelok valves. In series with the input valve was attached a critical orifice (50 ml/min flow at STP), so that the total volume of air sampled could be determined by timing (7 minutes flow = 350 ml STP sampled). The containers were then baked at 250° C to ensure complete outgassing of surface attached hydrocarbons while being flushed with carrier gas. The sample traps were sealed and pumped to a pressure of less than 6×10^{-6} Torr. These vacuum traps were placed in liquid nitrogen before air samples were taken. Final pressure in trap, after a 7-minute sample period, was less than 500 Torr.

The traps were returned to the laboratory and placed in the sample loop. The gas chromatograph was a Perkin-Elmer 900 equipped with dual flame ionization detectors, a 100-foot Scott OV-101 column, and liquid N_2 temperature programming at 4° C/min.

2. Data Collection

Two sites were selected by inspection of ERTS-1 imagery of the Great Dismal Swamp. These are shown in figure 2. Site One was termed Dismal and Site Two was termed Nansemond. Site One was located east of U.S. 17, east of Lake Drummond; Site Two was located north of the Dismal Swamp, adjacent to the Nansemond River.

Samples were obtained on 14 different dates (two taken sequentially except 6/10) for a total of 27 samples. All sampling was started at 10:30 A.M. local time. The Dismal site was sampled on five Mondays and four Tuesdays. The Nansemond site was sampled on three Thursdays and two Sundays. All samples were taken at six feet above the ground.

RESULTS

Table 1 lists the species, their type (P = paraffin, O = olefin, L = linear, C = cyclic, and # = number of carbons in molecule), the molecular weight (gms), the number of samples selected (non-zero entries), the average and standard deviation in ppb, and concentration in $\mu g/m^3$. It is estimated that these numbers are reliable to 20%.

Using all data available, there appears to be time dependence in the concentrations of pentane, mesitylene, α-pinene, cymene, β-pinene, limonene, myrcene, and cyclopentane. It should be noted that these have either 5 or 10 carbons per molecule. Very strong time dependence is evident only for cyclopentane.

Two molecules had bimodal concentration distributions which were time independent. These were 1-methyl cyclohexane and cineole.

since flame ionization detection was used, it is possible that, in both cases, other molecules with nearly the same elution time interfered with identification. This problem can be eliminated by adopting GC-mass spectrographic techniques.

Table 2 gives the concentrations by hydrocarbon families as well as the number of molecules identified for each family. Clearly paraffins represent the largest concentration at the two sites selected. Olefins are present at about 10% the concentrations of the paraffins. The aromatic (benzene ring based) species averaged about 50% of the olefins and about the same concentrations as the special plant generated C_{10} compounds.

Recently, Lonneman, Kopczynski, Darly, and Sutterfield (ref. 1) have sampled the hydrocarbon composition of urban air pollution for C_1 to C_{10} compounds. They give their results as ratios of sums of paraffins, olefins, and aromatics to acetylene for sites in the New York-New Jersey area. Our work did not attempt to measure acetylene, but since they give their toluene ratio and acetylene concentrations, it is possible to restructure their results for comparison.

Table 3 lists the concentrations (ppb carbon) of the sums of different hydrocarbon families; their 7 to 9 A.M. samples and our averaged 10:30 A.M. samples. Table 4 is similar but is for their samples at all times. Inspection of table 2 reveals that the Dismal Swamp total paraffin concentrations are much higher for the Dismal samples. This is true also for total olefins if 1-methyl cyclohexane is included in the analysis. As one would expect, the aromatics are much lower in the Swamp samples, since their primary source is thought to be antropogenically generated (transportation). Analysis of table 4 points out the same similarities with the C_5 paraffins, C_6 olefins, and aromatics. It is to be noted that the comparison data is C_1 - C_{10} data, while the Dismal Swamp data is C_5 - C_{10}. This fact points out the strong difference between the rural "clean" and urban "polluted" air masses. Even though the urban hydrocarbon concentrations are higher and the species variety are different

from those observed near the Dismal Swamp, still the "clean" rural air sampled in this study is loaded with paraffins and failed to reach the Primary Air Quality Standard.

Figure 3 is a plot of the concentration in ppb carbon versus carbon number (C_5 - C_{10}) for the average values shown in table 1. Recalling the problems of identification of 2 compounds (C_7 and C_{10}), these are plotted H, T, L, for highest values alone, total (high low of distribution), and lowest average values. Additionally, the C_{10} point reflects only cymene. It is a curious fact that the abundances appear to decrease exponentially with carbon numbers (slope 5/4). The same is true if one converts ppb carbon to $\mu g/m^3$ using molecule weights. (Slope is different.) At present, we have no explanation for this empirical result.

REFERENCE

1. Lonneman, W.A., Kopczynski, J.L., Darly, P.E., and Sutterfield, F.D. "Hydrocarbon Composition of Urban Air Pollution", Environmental Science & Technology, 8, 229 (1974).

Table 1. Hydrocarbon concentrations for each site and each sample.

Molecule	Type	Molecular Weight (gms)	No. of Samples Selected	Average (ppb) by volume	Stand Dev. (ppb) by vol	Concentration 25°C@1Atm (µg/m³)
N-pentane	PL5	72.15	14	2.72	1.51	8.01
2,2 dimethyl butane	PBL6	86.18	23	4.06	3.15	14.3
Isoprene	OBL5	68.13	18	1.31	.85	3.64
Pentene	OL5	70.14	9	5.86	4.94	16.8
Cyclopentane	PC5	70.14	27	188.00	80.00	538.00
Cyclopentene	OC5	68.13	7	2.1	2.5	5.84
2 Methyl Pentane	PBL6	86.18	24	16.1	4.8	56.6
3 Methyl Pentane	PBL6	86.18	21	1.9	1.5	6.68
N-hexane	PL6	86.18	24	3.1	2.1	10.9
1-hexene	OL6	84.16	24	7.4	7.1	25.4
Methyl Cyclopentane	PC6	84.16	26	24.2	9.4	83.1
1-Methyl Cyclopentene	OC6	82.16	25	1.3	0.76	4.4
Benzene	A6	78.12	23	2.1	1.1	6.7
Cyclohexane	PC6	84.16	20	11.1	6.0	38.1
Cyclohexene	OC6	82.15	25	5.5	1.8	18.4
N-heptane	PL7	100.21	21	1.3	0.90	5.3
Methyl Cyclohexane	PC7	98.15	25	1.2	0.81	4.8
Toluene	A7	92.15	22	4.3	2.3	16.2
Octane	PL8	114.23	21	1.2	0.7	5.6
Methyl Cyclohexene	PC*7	96.17	10L	7.6	3.2	29.8
			9H	42.5	7.8	166.8
			19T	24.2	18.9	95.00
Ethyl Benzene	A8	106.17	23	1.7	1.1	7.37
mtp Xylene	A8	106.17	8	0.5	0.2	2.17
O Xylene	A8	106.17	26	0.74	0.26	3.20
Cymene	A10	134.22	18	0.55	0.23	3.0
α-Pimene	U10	136.24	24	6.5	4.0	36.1
Mesitylene	A9	120.2	23	0.88	0.66	4.32
β-Pinene	U10	136.24	21	0.96	0.51	5.3
Myrcene	A?10	136.24	23	5.3	2.9	29.5
Limonene	C10	136.24	17	0.70	0.45	3.9

Table 2. Concentrations for various hydrocarbon families.

	ppb carbon	Number of molecules
ΣParaffins	255	
ΣC_5 Paraffins	190	2
ΣC_6 Paraffins	60.3	6
ΣC_7 Paraffins	2.5	2
ΣC_8 Paraffins	1.2	8
ΣOlefins	23.4*	
ΣC_5 Olefins	9.3	3
ΣC_6 Olefins	14.2	3
ΣC_7 Olefins	*	*
ΣAromatics	10.8	7
Toluene	4.31	
ΣC_8 Aromatics	2.94	3
ΣC_{9+10} Aromatics	1.43	2
ΣC_{10} Specials	8.16	3**

* excludes 1 methyl cyclohexane (24.2, 42.6, 7.6)
** excludes cineole (19.6, 43.9, 5.1)

Table 3. Comparison of rural and urban concentrations of hydrocarbon values (morning values).

TOTAL CONCENTRATION ppb CARBON

7 to 9 A.M.

	Dismal Swamp	Bayonne New Jersey	Linden New Jersey	Manhattan New York	Brooklyn New York
ΣParaffins	255	90.7	135	190	159
ΣC_5 Paraffins	190	31.1	40	64	48
ΣOlefins	23.4*	26	44.7	60.3	48
ΣC_6 Olefins	14.2	0.36	0.91	0.67	1.23
ΣAromatics	10.8	55.4	78.7	136	135
ΣC_8 Aromatics	2.9	23.2	32.2	67.5	57.7
ΣC_{9+10} Aromatics	1.4	10.9	16.1	22.7	26

* excludes 1 methyl cyclohexane (24.2, 42.6, 7.6)

Table 4. Concentrations of hydrocarbon families for all times.

TOTAL CONCENTRATION ppb CARBON

All Times

	Dismal Swamp	Bayonne New Jersey	Linden New Jersey	Manhattan New York	Brooklyn New York
ΣParaffins	255	310	413	372	362
ΣC_5 Paraffins	190	103	123	126	103
ΣOlefins	23.4*	77	125	96	95
ΣC_6 Olefins	14.2	1.65	3.15	2.17	1.53
ΣAromatics	10.8	203	254	294	363
ΣC_8 Aromatics	2.9	93.4	106	117	150
ΣC_{9+10} Aromatics	1.4	26.5	43	83	60

* excludes 1 methyl cyclohexane (24.2, 42.6, 7.6)

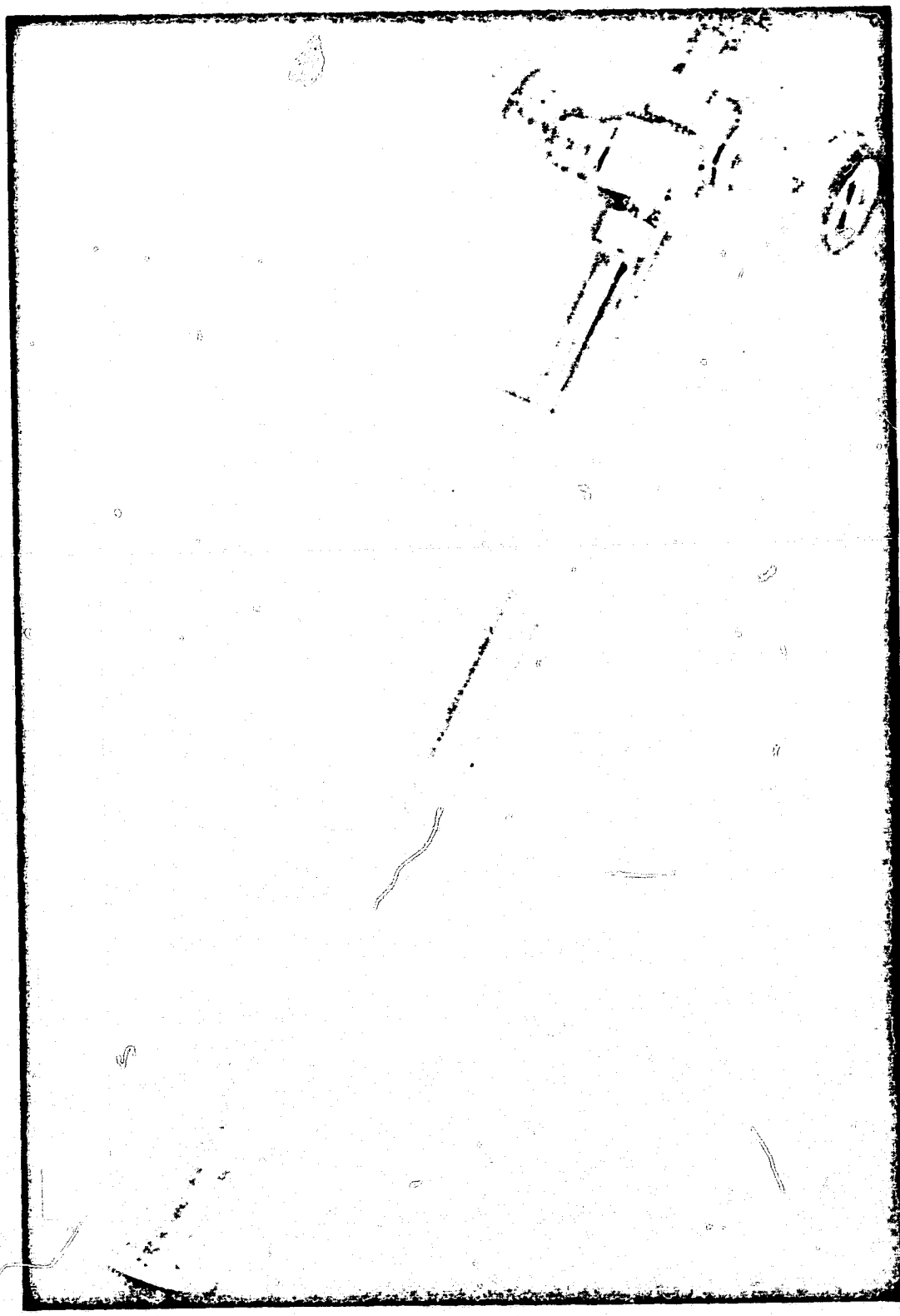

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Figure 1. Stainless steel air sampling bottle.

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Figure 2. ERTS-1 (LANDSAT-1) image of Dismal Swamp.

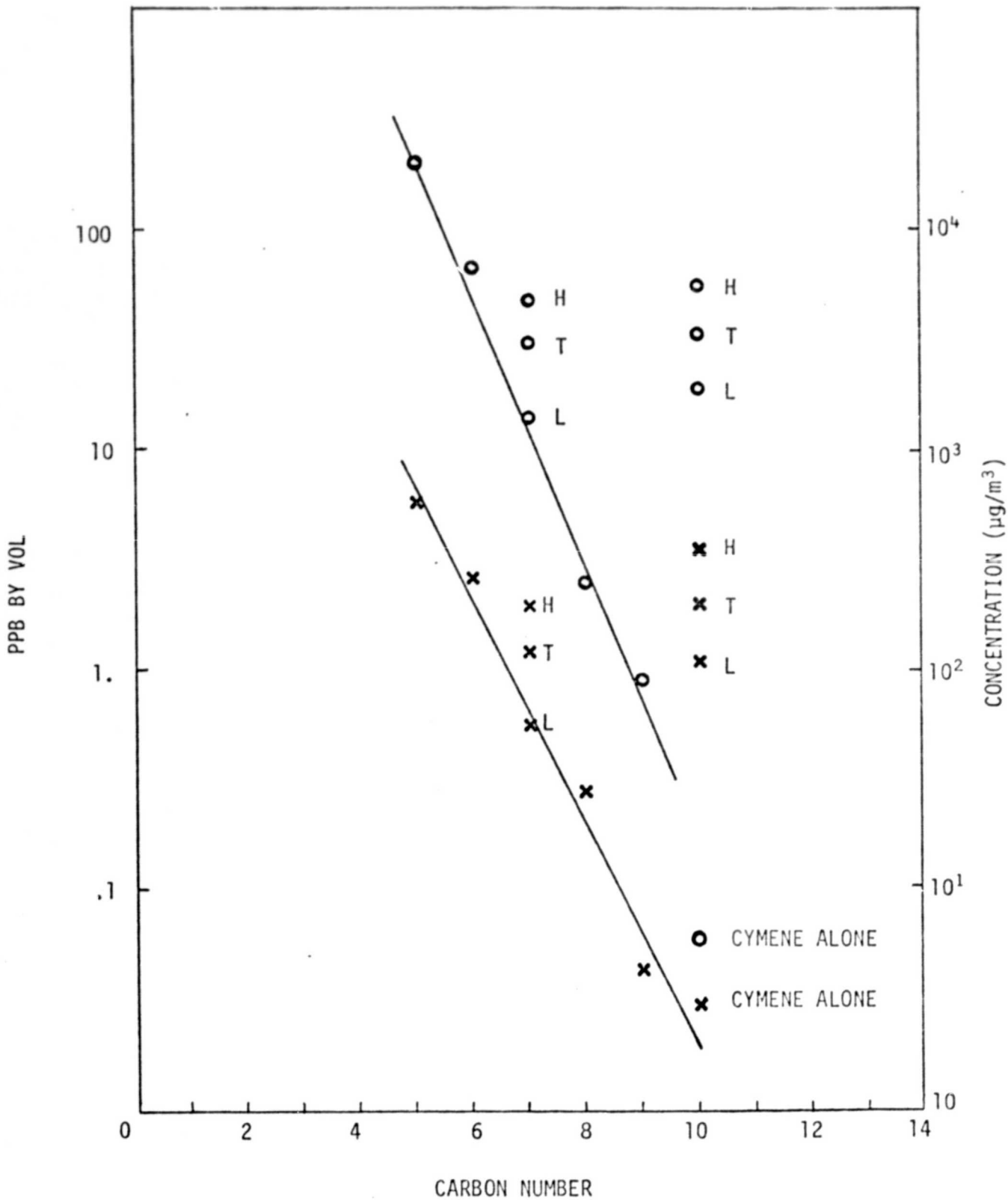
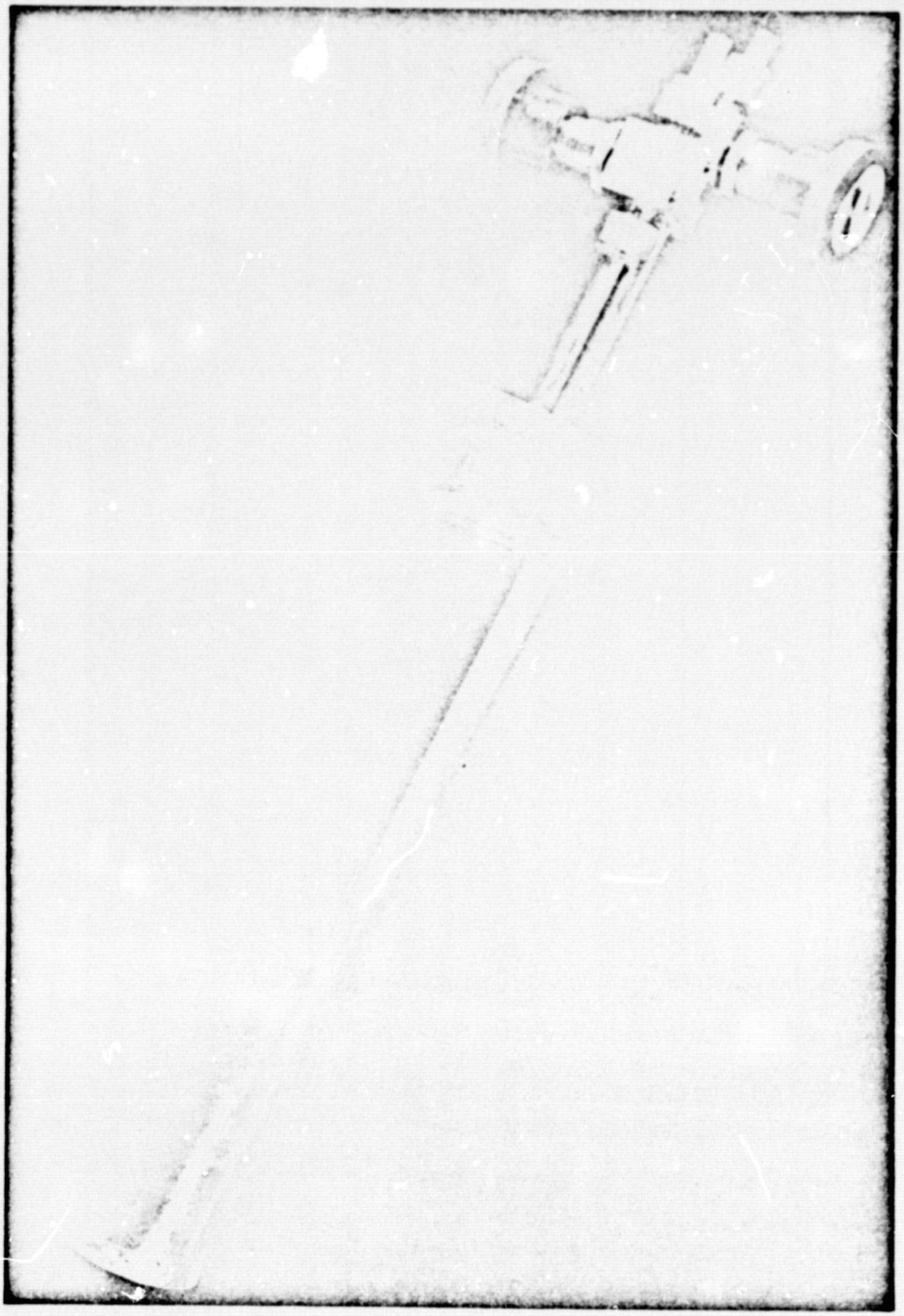


Figure 3. Plot of average concentration versus carbon number.



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